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Technical Communication

Performance characteristics of a miniaturised chemical looping steam reformer for hydrogen enrichment of fuels

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ABSTRACT

A miniaturised chemical looping steam reformer (μ -CLSR) is being developed at the University of Newcastle (Australia) for onboard hydrogen enrichment of fuels in internal combustion engines. Experimental results from the first prototype highlighted an imbalance between the rates of redox reactions. A new configuration has been developed to resolve this shortcoming. The objective of this study is to examine the effectiveness of the new configuration in handling the imbalance between redox rates. Experiments were conducted on magnetite and wuestite metal oxides under methane and steam environments in the new configuration. Results indicate that if micro-reactors within the reformer are operated in parallel during the oxidation half cycle and in sequence during the reduction half cycle, the imbalance can be effectively managed. This combined with manifold switching of reacting gases at 48 s intervals enables metal oxides to achieve a 30% fractional conversion at 900 °C; resulting in a product gas stream with 96% H₂ purity.

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1. Introduction

Hydrogen enrichment of fuels (i.e. addition of small quantities of H₂ into a premixed air/fuel mixture) can greatly extend the lean and dilution limits of the air/fuel mixtures; leading to significant improvements in the thermal efficiency and emission reductions of combustion systems. It is therefore not surprising that the implementation of the hydrogen enrichment concept in applications as diverse as gas turbines [1], liquid and/or gas fired boilers [2], micro-combustors [3], and internal combustion engines (ICE) [4–7] has been a subject of great interest over the past two decades. Development of

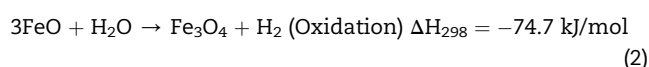
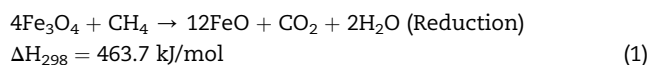
onboard fuel reformers for hydrogen enrichment of fuels in ICEs has been particularly an active area of research. A variety of catalytic reformers have been developed for this purpose. However, these reformers have achieved a limited degree of success because of their [8]: (i) inability for production of high purity H₂, (ii) unwanted fluctuations in the rate and composition of the product gas stream especially when the ICE is under load, and (iii) large physical dimensions and heavy weights.

To resolve the above shortcomings a novel fuel reformer is being development at the University of Newcastle (Australia) for ICE applications based on the chemical looping steam

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reforming (CLSR) [9–11] and process miniaturisation [8,12,13] principles. Miniaturisation of the CLSR concept (μ -CLSR) lowers the overall size/weight of the system but more importantly enables the fuel reformer to generate high purity hydrogen and avoid fluctuations in the composition of the product gas. Therefore, compared with conventional fuel reformers, μ -CLSR provides a more effective control over H_2 production under load [8]. The working principle of the μ -CLSR is based on a two-step redox cycle shown below:



The μ -CLSR system incorporates a pair of identical micro-reactor assemblies with plate/stack architecture where each assembly comprises a number of “Units” (reactor plates) with planner structures stacked on top of each other. Each unit, in turn, consists of zigzag shaped micro-reactors [8]. The system has a modular configuration and, as such, the number of assemblies, units and micro-reactors can be adjusted to suit any desired throughput. Unlike conventional chemical looping systems, carrier particles are not circulated between the two reactor assemblies. Instead, micro-reactors are packed with metal oxide (MeO) particles and a typical redox cycle is completed by switching the reactant gases from one reactor assembly to the other rather than circulating the particles. In this “manifold switching (MS)” approach each assembly functions periodically as a fuel reactor and a steam reactor; avoiding the particle transport issues inherent to conventional chemical looping systems [8]. Our preliminary investigations of a prototype μ -CLSR have confirmed the technical feasibility of the concept and resulted in the following key findings [8]:

- During the reduction step and for Fe_3O_4 fractional conversions between 0 and $\sim 60\%$, the corresponding methane conversion is relatively small and as such the methane concentration in the product gas mixture remains high (see Figure 12 in Ref. [8]).
- For Fe_3O_4 fractional conversions greater than 60% the methane conversion in the product gas sharply decreases due to catalytic effect of FeO (formed during Fe_3O_4 reduction) on methane decomposition process (see Figure 12 in Ref. [8] or [14]).
- In contrast, during the oxidation step the hydrogen concentration in the product gas stream sharply increases over the FeO fractional conversions between 0 and $\sim 30\%$; reaching a maximum of about 98% at a fractional conversion of 30%. Beyond this point, the concentration of hydrogen in the products rapidly diminishes (see Figure 12 in Ref. [8]). FeO could also be reduced by H_2 at temperature as high as 900°C , and thus there could be a mixture of Fe, FeO, and Fe_3O_4 in the reactor.
- Rates of redox reactions at 900°C are notably higher than those at 800°C and 700°C .
- The rate of oxidation (FeO to Fe_3O_4) is much slower than the rate of reduction. For instance, as shown in Figure 13 of

Ref. [8] (repeated here for convenience as Fig. 1), at a temperature of 900°C the conversion time for 80% reduction is almost a quarter of that corresponding to 80% oxidation.

Of these, the imbalance between the rates of redox reactions outlined in point “e” poses a challenge to the smooth operation of the fuel reformer; representing a technical issue which ought to be resolved. A new system configuration is proposed here to overcome this technical issue (Section 2) and the present paper provides a preliminary assessment of the new configuration.

2. New configuration for the μ -CLSR prototype

The imbalance between the rates of reduction and oxidation outlined in Section 1 can be an impediment to the operation of the μ -CLSR system if not properly alleviated. The imbalance can be managed if over the same period of time metal oxide particles attain the same level of conversion during both reduction and oxidation steps. This is achieved in the present study using a μ -CLSR specifically configured for multi-stage operation. The configuration is shown schematically in Fig. 2. As shown, both micro-reactor assemblies comprise 4 micro-reactor units each consisting of 17 zigzag shaped micro-reactors (0.05 m long with a cross sectional area of $200 \times 100 \mu\text{m}^2$) arranged in parallel formation. All micro-reactors are initially packed with FeO particles. As highlighted in Fig. 2, the micro-reactor units within each assembly are operated in sequence during the reduction step (Fe_3O_4 to FeO) and in parallel during the oxidation step. For a reaction temperature of 900°C the manifold switching is enforced at 48 s intervals. As a result, during the oxidation step (i.e. parallel operation) the residence time for metal oxide particles is 48 s and, thus, they should reach a nominal fractional conversion of about 30% (see Fig. 1). This level of conversion is preferred because it corresponds to the highest concentration of H_2 in the product gas stream (see key finding “c” in Section 1 or Figure 12 in Ref. [8]).

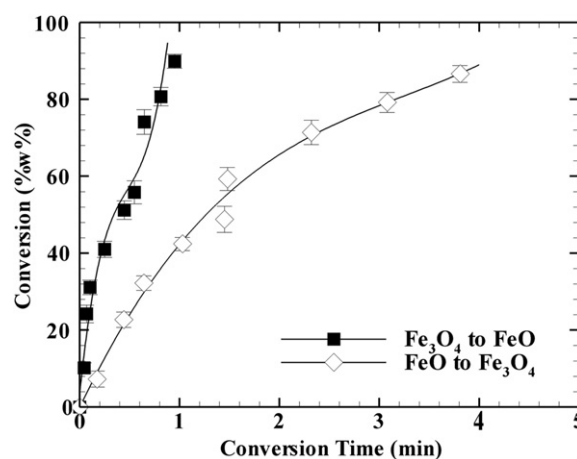


Fig. 1 – Fractional conversion of metal oxides at 900°C during reduction and oxidation steps in the μ -CLSR setup [8].

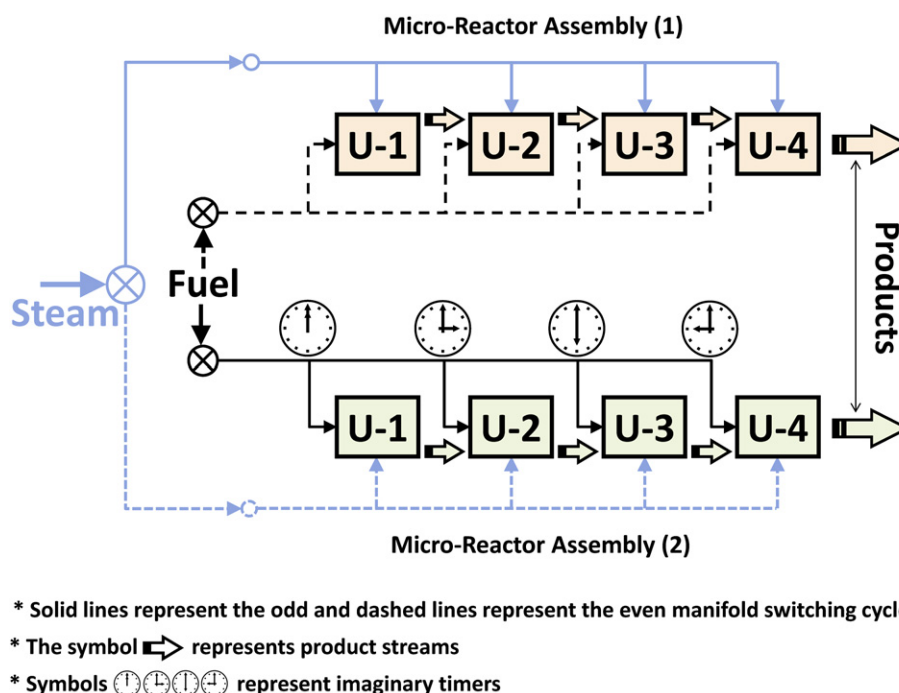


Fig. 2 – Schematic representation of the new configuration for the μ -CLSR fuel reformer.

However, a 30% conversion during the oxidation step implies that after manifold switching and at the beginning of the reduction step the micro-reactors in the reduction side of the reformer approximately contain 30% Fe_3O_4 and 70% FeO particles. Therefore, only 30% of the weight of metal oxide particles within each micro-reactor (that of Fe_3O_4) would be convertible during the reduction step. Referring to Fig. 1, it can be seen that the conversion time for 30% reduction is roughly 12 s. Since the time interval between consecutive MS cycles is greater than 12 s (in fact 48 s), the micro-reactor units during the reduction step have to be operated in succession so that the overall residence time becomes equal to the MS interval. That explains why the configuration adopted here for the reduction step comprises 4 reactor units in series (i.e. $4 \times 12 \text{ s} = 48 \text{ s}$). In this formation, fuel is supplied to micro-reactor units U-1, U-2, U-3 and U-4 over the first; second; third and fourth quarters of the MS interval, respectively (see the imaginary timers in Fig. 2). The outlets of all micro-reactor units empty to a common exhaust for the whole assembly. The above configuration ensures that both reactor assemblies achieve the same level of conversion within a typical 48 s manifold switching interval.

3. Experimental

A comprehensive series of experiments were conducted at 900 °C on magnetite and its reduced form (wuestite) using a new μ -CLSR prototype with a design similar to that illustrated in Fig. 2. The selection of 900 °C temperature was based on previous findings (see key finding “d” in Section 1). Methane was used as the fuel source in all experiments and

metal oxide samples were prepared by co-precipitation method following the procedure outlined in our previous publications [8,15–17]. The experimental setup was similar to that used in our earlier work [8]. For each set of experiments at least three MS cycles were repeated to ensure the integrity and accuracy of collected data from a statistical point of view. A series of uncertainty analyses was also carried out on the experimental data and the results have been incorporated into Fig. 3 and Fig. 4 as error bars. The approach described by Haile was used to calculate uncertainties for a 95% confidence level from standard deviations [18].

4. Results and discussion

Fig. 3 provides a summary of experimental results corresponding to the oxidation step. While Fig. 3 a shows plots of metal oxide conversion against time for a typical MS interval (i.e. 48 s), Fig. 3 b and c present volumetric concentrations of steam and H_2 in the product gas stream, respectively. Apart from the experimental data, trend lines have also been shown in Fig. 3. As can be seen, despite the scatter in the data all four micro-reactor units (U-1 to U-4) exhibit a similar performance. Fig. 3 a, in particular, indicates that 30% conversion is achievable within a typical 48 s MS interval; confirming that the new configuration can indeed deliver the desired conversion level [8]. However, the relationship between the metal oxide conversion and time appears to be non-linear. As such within the first 10 s the conversion rises from 0 to about 10% while it takes another 20 s before the conversion doubles up to 20%. A comparison between Fig. 3 b and c shows that nearly 90% of steam is converted to hydrogen within the first half of

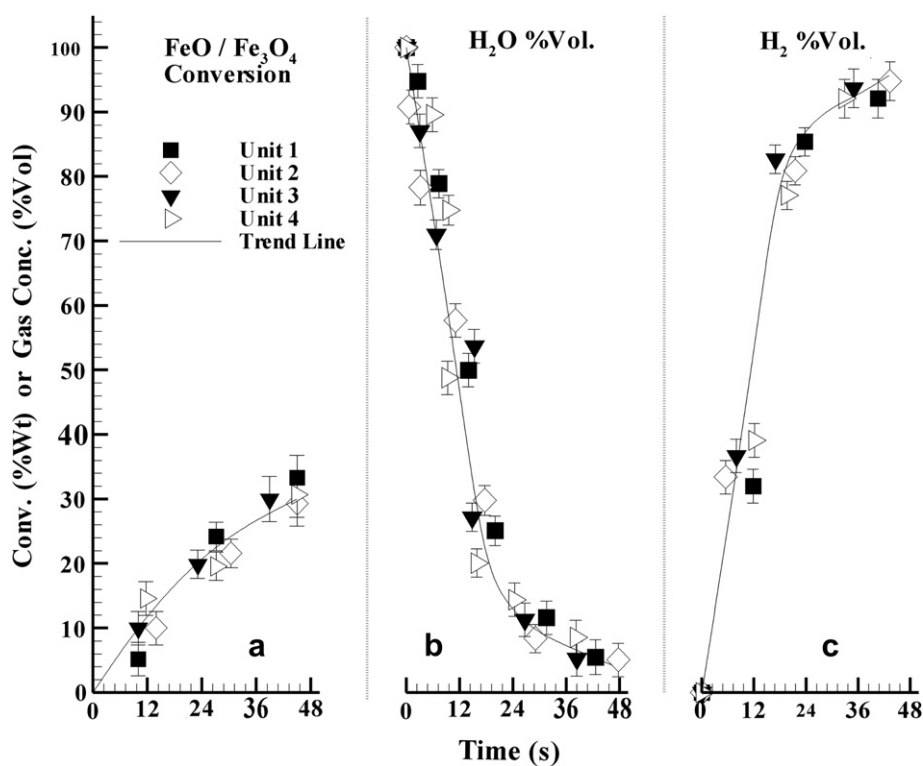


Fig. 3 – Experimental data corresponding to oxidation step plotted as a function of time for a single MS interval; (a) FeO to Fe₃O₄ conversion, (b) H₂O volumetric concentration in the product gas stream, and (c) H₂ volumetric concentration in the product gas stream.

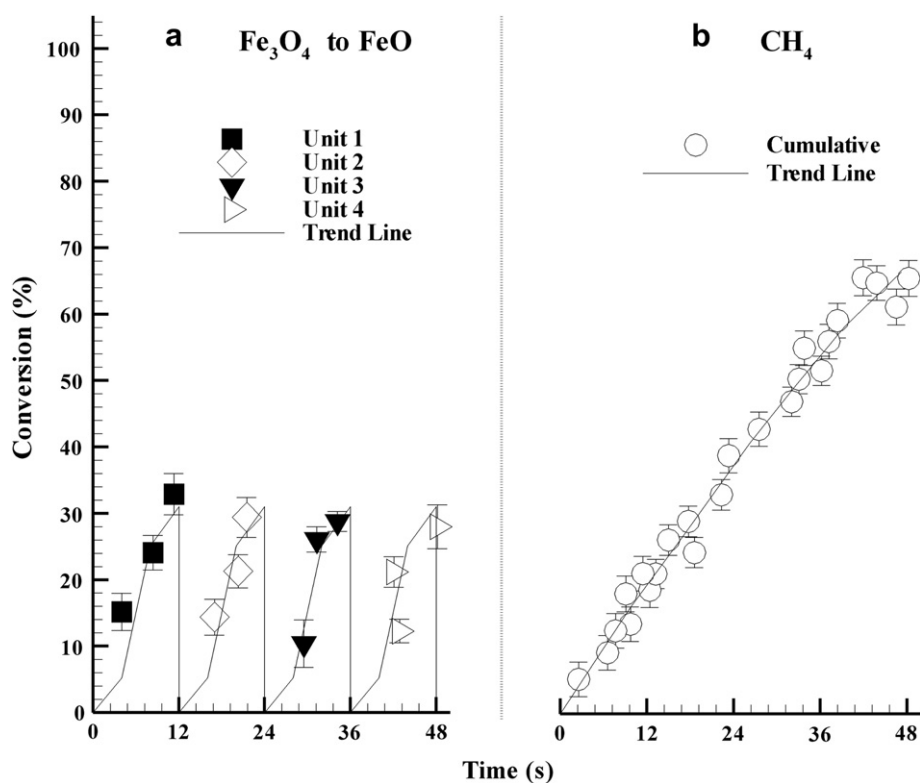


Fig. 4 – Experimental data corresponding to reduction step plotted as a function of time for a single MS interval; (a) Fe₃O₄ to FeO conversion, and (b) cumulative methane conversion.

the MS interval. The conversion then slows down rapidly and plateaus over the second half of the MS interval. Consequently, the maximum achievable H_2 concentration in the product gas stream is about 96% which is slightly lower than what was achieved in our previous work ($\sim 98\%$, see Ref. [8]).

Fig. 4 summarises the experimental results corresponding to the reduction step. Fig. 4 a shows plots of Fe_3O_4 to FeO conversion over a MS interval while Fig. 4 b illustrates cumulative conversion of methane over the same period. Fig. 4 a clearly illustrates the sequence of reduction in U-1 to U-4 over their respective 12 s intervals and indicates that despite obvious differences, all reactor units are capable of attaining the desired 30% reduction within the designated 12 s. This highlights the ability of the new configuration in managing the imbalance in redox rates.

The data sets presented in Fig. 4 b have been obtained from the measurements of methane concentration in the common exhaust of the micro-reactor assembly and, as such, represent the cumulative values. As can be seen, the methane conversion approximately follows a linear trend and for every 12 s of operation 17% conversion is accomplished. Whilst, this figure is a little higher than the values obtained in our earlier study under identical conditions ($\sim 15\%$ CH_4 conversion), the figure still represents a modest conversion for methane. To a large extent, methane conversion is limited by the fractional conversions of the metal oxides under conditions prevailing in the μ -CLSR prototype ($\sim 30\%$ here). We previously showed [8] that the concentration of methane in the product gas gradually decreases as a function of metal oxide conversion. This trend continues over the range of metal oxide fractional conversions less than 60%. Higher methane conversions can only be accomplished for metal oxide fractional conversions greater than 60%. At this point a sharp increase in the slope of the plot of methane volumetric concentration versus metal oxide fractional conversion (key finding 'b' in Section 1) takes place which can be attributed to catalytic effect of FeO on methane decomposition. This particular catalytic effect has obviously no bearing on the results presented here considering the operational requirements imposed on the μ -CLSR prototype and measures put in place to meet these requirements have limited the metal oxide conversion to 30% for which the above catalytic effect is negligible. That explains why relatively modest methane conversions were achieved in this study.

5. Conclusions

A comprehensive series of experiments were carried out to assess the technical viability of a modified version of the μ -CLSR system reported in our earlier work [8] for hydrogen enrichment of fuels. The modifications made to the system were in response to the issues identified previously and specifically aimed at resolving the imbalance between the rates of redox reactions taking place within the two micro-reactor assemblies of the fuel reformer. Experimental results indicate that a configuration in which the micro-reactor assemblies are operated in parallel during the oxidation step (i.e. FeO to Fe_3O_4 in steam) and in sequence during the reduction step (Fe_3O_4 to FeO in methane) can effectively

resolve the above imbalance. This configuration combined with manifold switching of reacting gases at nominal 48 s intervals enables metal oxides to achieve a 30% fractional conversion at $900^\circ C$; resulting in a product gas stream with 96% H_2 purity.

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